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G.P. Gaidar

Effect of Thermal Annealings and Cooling Methods on Electrophysical Parameters of n-Si, Doped with Phosphorus Impurity via the Melt and by Nuclear Transmutation Technique

Institute for Nuclear Research of NAS of Ukraine, 47, prospect Nauky, 03680 Kyiv, Ukraine, e-mail: gaydar@kinr.kiev.ua

The effect of the different regimes of heat treatment on the kinetics of electronic processes in silicon crystals doped with phosphorus impurity via the melt and by nuclear transmutation technique is researched. The most significant influence of cooling under intermediate value of cooling rate ($u_{cl} \approx 15\ ^{o}$C/min) after high-temperature annealing on the main electrophysical parameters of the transmutation-doped n-Si ⟨P⟩ crystals was established. Features of changes of the anisotropy parameters of mobility and thermal electromotive force measured on silicon crystals of different doping techniques both in the initial state, and after high-temperature annealing when using different cooling rates, were found and explained.

Keywords: electrophysical parameters, n-silicon, doping techniques, anisotropy parameters, thermal annealing, cooling rate.

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Introduction

At present, and probably in the next decade, the elementary semiconductors will remain the profiling material of electronic technology [1-3]. Thus, the ultra-high purity germanium, due to transparency in the infrared region of the spectrum, is widely used in the production of elements of infrared optics: lenses, prisms, optical windows of sensors, etc. [4-6]. The ultra-large and ultra-fast integrated circuits, new elements of microelectronics are created on the basis of silicon, which is the most convenient and cheap semiconductor material thanks to considerable natural reserves of raw materials [7-9].

In the technology of manufacturing semiconductor devices (especially in planar technology), a number of thermal anneals are used at different stages of their readiness, and the conditions, under which the corresponding semiconductor objects are cooled from the annealing temperature, can differ substantially. Therefore both in the scientific respect and for practical applications in electronics, it was of interest to investigate the effect of not only the annealing temperature, but also the cooling rate of the samples on the kinetic coefficients in silicon single crystals.

In addition, when creating devices of modern solid-state electronics, an equally important technological method is the doping of semiconductors with necessary impurities to the required concentrations, which makes it possible to change the properties of materials in a directional manner [10, 11]. Into the forbidden band of semiconductor the impurity atoms introduce the local levels, which act as suppliers of electrons in the conduction band (donors) or traps for them, ensuring the appearance of holes in the valence band (acceptors), or play the role of centers of radiative or nonradiative recombination of the nonequilibrium charge carriers [12, 13]. Impurity atoms are introduced into the volume of ingots or layers at different stages of growth in order to purposefully change their resistivity and form the necessary structures. For this purpose a fairly wide range of methods has been developed and mastered, the main ones being the following: introduction of an impurity into a melt or gas medium during the growth of crystals and films; diffusion of impurities from surface sources; the introduction of an impurity from a beam of accelerated ions [14-16].

At the initial stage of development of solid-state electronics, the mentioned methods quite satisfied to the level of those problems that arose at that time. However in the conditions of further complication of semiconductor devices, the serious limitations of the traditional methods were revealed, primarily, due to the material inhomogeneities and structural defects of the crystal, which were manifested during diffusion and in other technological operations. One of the fundamentally important ways to improve the quality of semiconductor crystals is the development and practical mastery of methods for their doping, which could provide a homogeneous distribution by volume of doping impurities while maintaining the structural perfection of the crystal [17, 18].

In connection with this, one of the important directions of the technology of obtaining homogeneous (by the distribution of the phosphorus impurity) silicon crystals deserves attention – the method of transmutation doping [19]. In this case, the dopant phosphorus is introduced into the silicon volume at the expense of nuclear transmutation, that is, by irradiating of high-purity Si [grown by the method of crucible-free zone melting] with the flux of slow (thermal) neutrons. In the volume of irradiated crystals, the silicon atoms are converted into the phosphorus atoms in accordance with the nuclear reaction $^{30}\mathrm{Si}\left(\mathrm{n},\gamma\right)\,^{31}\mathrm{Si}\xrightarrow[2.62\,\mathrm{h}]{\beta^{-}}\,^{31}\mathrm{P}$ [20]. Irradiation of silicon by thermal neutrons is also accompanied by irradiation with fast neutrons and gamma component of the reactor spectrum. As a result, the silicon single crystals, saturated with radiation defects, are obtained. In addition, after irradiating of silicon with neutrons from a nuclear reactor, the ^{31}Si atoms (which spontaneously transfer to ^{31}P) are, as a rule, in the interstitial positions. Such positions correspond to electrically inactive states. To anneal the radiation defects and activate the ^{31}P atoms, which exhibit donor properties in the Si volume only at the lattice sites, the transmutation-doped silicon is necessarily subjected to so-called technological annealing (at the annealing temperature $T_{ann} = 800 \div 850$ °C during $1 \div 2$ h) [21].

As the experiment showed [22], the transmutation-doped crystals differ from ordinary crystals (grown by the Czochralski method and doped with phosphorus impurity through the melt) by the increased homogeneity in the distribution of the dopant over the volume of the crystal. In this connection, the question arises whether similar advantages are found in the transmutation-doped Si crystals, as compared with conventional crystals, when the phenomena associated with the scattering of phonons, rather than electrons, will be used as trial phenomena. Such methodological approach (in the case of its effectiveness) will be equivalent, in principle, to expanding the possibilities of the procedure, since the de Broglie wavelength of phonons satisfies the inequality $\lambda_{ph} \ll \lambda_e$.

The aim of this work was the investigation of the effect of various types of heat treatment [temperature, duration of thermal annealing, cooling rate of crystals from the annealing temperature to the room temperature] on the most important electrophysical and thermoelectric parameters [majority-carrier concentrations, their mobilities, anisotropy parameters of mobility and thermoelectromotive force (thermo-emf)] in the n-Si crystals of different technological origin.

I. Changes in the electrophysical parameters of dislocation-free n-Si <P> crystals, stimulated by thermal annealings

The investigated dislocation-free silicon crystals were cut out so that the current vector $\vec{J}$ in the samples was in the plane of the growth layers, which eliminated the need to take into account the effect of the growth layers when analyzing the results obtained.

For the experiments, samples with different contents both the doping impurity of phosphorus, and the residual impurity of oxygen were used. The samples were selected according to the principle of similarity (or substantial distinction) in their specific resistance (or charge carrier concentration) from among of grown both by the Czochralski method (Cz) and by the method of crucible-free zone melting (FZ). Also, the specificity of doping with phosphorus impurity (via the melt or by nuclear transmutation technique) was taken into account.

For investigated samples in Tables 1 and 2 are given (for 300 and 77.4 K) both the initial data about charge carrier mobilities (μ) and their concentrations (n_e), obtained before the thermal annealing, and the data obtained on the annealed samples at different cooling rates ($\upsilon_{cl} \approx 1$ and 1000 °C/min). The annealing at $T_{ann} = 1200$ °C during $t = 2$ h was carried out in a vacuum. With a rapid cooling ($\upsilon_{cl} \approx 1000$ °C/min), the samples from the furnace where the annealing was performed were discharged into a bath with transformer oil of room temperature, and at a slow cooling ($\upsilon_{cl} \approx 1$ °C/min) the samples were cooled together with the furnace.

Under thermal annealings with slow and rapid cooling, a tendency was observed to decrease of the charge carrier concentration n_e, which is characteristic both for low-resistance ($\rho_{300\mathrm{K}} \approx 0.5$ Ohm·cm), and for high-resistance ($\rho_{300\mathrm{K}} \approx 80$ Ohm·cm) samples (see Table 1). At the same time, changes in the mobility values at the single-type annealings of these crystals were oppositely directed: the mobility in low-resistance samples showed a tendency to increase, and in high-resistivity samples – to decrease. Probably, an increase in the charge carrier mobility after high-temperature annealing in the low-resistance crystals is associated with the temperature "destruction" of thermodonors in samples enriched with an oxygen impurity (Table 1).

In the group of samples with a raised content of the residual oxygen impurity [$N_{\mathrm{Oi}} \approx (2 \div 5) \cdot 10^{17}$ cm^{-3})], the presence of the deeper energy level was characteristic for the low-resistance crystals in comparison with that, which was in the slightly doped crystals (with the same phosphorus impurity). The evidence of this is a strong decrease (approximately 2.5 times) in the concentration n_e at the transition from measurements at 300 K to measurements at 77.4 K that was not observed in the case of higher resistance samples.

The changes in the charge carrier concentration with thermal annealings in crystals with a lower content of residual oxygen impurity [$N_{\mathrm{Oi}} \approx (5 \div 10) \cdot 10^{15}$ cm^{-3}] turned out less noticeable (see Table 2). Since the level

Table 1

Changes in the electrophysical parameters of n-Si ⟨P⟩ with an increased content of the residual oxygen impurity [$N_{Oi} \approx (2 \div 5) \cdot 10^{17}$ cm^{-3}] under the influence of thermal treatments

Method of crystal growth	T, K	Thermal annealing (1200 °C, 2 h) and cooling	ρ_{300K} = 0.5 Ohm·cm		ρ_{300K} = 80 Ohm·cm	
			$n_e \cdot 10^{-15}$, cm^{-3}	μ, cm^2/V·s	$n_e \cdot 10^{-13}$, cm^{-3}	μ, cm^2/V·s
n-Si ⟨P⟩, Cz in the argon atmosphere	300	Before thermal annealing	8.76	1380	4.80	1840
		1 °C/min	8.64	1360	3.90	1680
		1000 °C/min	8.46	1420	3.00	1760
	77.4	Before thermal annealing	3.66	8050	5.38	20100
		1 °C/min	3.49	8270	4.30	19300
		1000 °C/min	3.44	9580	2.64	19800

Table 2

Changes in the electrophysical parameters of n-Si ⟨P⟩ with a reduced content of the residual oxygen impurity [$N_{Oi} \approx (5 \div 10) \cdot 10^{15}$ cm^{-3}] under the influence of thermal treatments

The growth and doping method of crystal	T, K	Thermal annealing (1200 °C, 2 h) and cooling	$\rho_{300K} \approx$ 15 Ohm·cm	
			$n_e \cdot 10^{-14}$, cm^{-3}	μ, cm^2/V·s
n-Si ⟨P⟩, FZ in the argon atmosphere	300	Before thermal annealing	2.10	1790
		1 °C/min	2.49	1710
		1000 °C/min	2.68	1670
	77.4	Before thermal annealing	2.78	18400
		1 °C/min	2.51	18050
		1000 °C/min	2.54	17350
n-Si ⟨P⟩ doped by nuclear transmutation technique	300	Before thermal annealing	2.28	1670
		1 °C/min	2.67	1730
		1000 °C/min	2.60	1700
	77.4	Before thermal annealing	2.38	17100
		1 °C/min	2.30	17950
		1000 °C/min	2.20	17800

of the dopant in the crystals of Table 2 does not coincide with the charge carrier concentration n_e both of high-resistance, and low-resistance samples from Table 1, then when analyzing the results of Table 2 it makes sense to compare the data for the crystals, which belong only to this table.

It turned out that the tendencies in the change of mobility after thermal annealings in crystals doped in the ordinary method and by transmutation are oppositely directed: in the ordinary crystals there is a tendency to decrease of mobility (as can be seen from Table 2), whereas in the transmutation-doped samples there is a tendency to insignificant growth. This statement remains valid for experiments conducted both at 300 K, and at 77.4 K. The increase in mobility after thermal annealing of transmutation-doped samples is associated with a more complete annealing (at 1200 °C) of those defects that were not completely eliminated by standard technological annealing. Such annealing enters as separate procedure into the technology of neutron transmutation doping.

Studies carried out using high-resolution electron microscopy showed that the precipitates, which formed in silicon crystals with the residual oxygen impurity at thermal annealings, have the amorphous structure $(SiO)_x$ [23].

The formation of plate-like precipitates is observed up to T_{ann} = 1000 °C. With an increase in T_{ann} from 600 to 1000 °C, their concentration decreases from 10^{11} to 10^{7} cm^{-3}, however the precipitate size increases from 1.5 to 1000 nm [23, 24].

At higher T_{ann} = 1200 °C the large plate-like precipitates are formed, which consist from an amorphous SiO_x phase. The formation of oxygen precipitates leads to the occurrence of mechanical stresses due to the difference in the molecular volumes of the Si oxide and the matrix. These stresses can be partially reduced at the expense of the emission of interstitial Si atoms from the precipitate into the matrix. Consequently, a decrease in the degree of saturate of the solid solution of oxygen in silicon (at the expense of oxygen precipitation) leads to the saturate of the silicon matrix by the intrinsic interstitial atoms. The number of silicon atoms, emission-embedded in the interstitial space

Table 3

Effect of different cooling rates after high-temperature annealing on the main Hall parameters of transmutation-doped n-Si ⟨P⟩ crystals

Conditions of thermal annealing and cooling		r, Ohm·cm	$n_e \cdot 10^{-13}$, cm^{-3}	$m_{77.4K}$, cm^2/V·s
T_{ann} and the annealing duration	u_{cl}, ^{o}C/min			
1200 ^{o}C, 2 h	1000	4.62	6.61	20500
	15	9.18	3.60	18800
	1	5.55	5.66	20100
The initial crystals		4.56	6.42	21400

of the crystal lattice as a result of the addition of one oxygen atom to the precipitate, can be calculated from the formula [23]

$$b = \frac{d_{Si} - d_{SiO_2}}{2\ d_{SiO_2}} \cong 0.5\,, \qquad (1)$$

where d_{Si} and d_{SiO_2} are the molecular densities of Si and SiO_2, respectively.

The formation of dislocation loops from the interstitial Si atoms is accompanied by a decrease in the local mechanical stresses of the crystal lattice.

If the oxygen-containing Si crystal before the high-temperature thermal annealing has been subjected to preliminary low-temperature annealing (or has undergone it during the growing process), then in such crystal there will already be germinal centers of crystallization. This circumstance at high annealing temperatures will significantly effect on the morphology of the precipitates, which causes a change in their shape from plate-like to bulk polyhedrons (usually in the form of truncated octahedra [24] with faces parallel to the $(111)_{Si}$ plane [23]). Precipitates formed during the thermal annealing in the 1200 °C region have a size spread within the limits of 15 ÷ 20 nm (0.015 ÷ 0.020 μm) to 0.1 μm. Consequently, we have every reason to consider these precipitates (with their local surroundings in the form of a mechanically-stressed crystal lattice together with gettered atoms of impurities) as Herring's type inhomogeneities that are statistically distributed throughout the volume of the crystal [25].

II. Effect of high-temperature annealing and different cooling rates on Hall parameters of transmutation-doped n-Si áPñ crystals

To make the experiment, we used transmutation-doped samples of n-Si ⟨P⟩ based on the following considerations: the distribution of the phosphorus impurity atoms in such crystals is more homogeneous and, in addition, it is this material that is profiling in planar industrial technology, where similar thermal anneals are widely used. The experiment was carried out on slightly doped silicon crystals, because in such crystals the measured parameters will be large in absolute value and, therefore, can be measured with a smaller error.

Typical results of these experiments, carried out on three series of transmutation-doped silicon samples (by 4 samples in each series) followed by averaging, are given in Table 3. As can be seen from Table 3, even samples cut from the same ingot and, therefore, grown, doped and annealed under identical conditions, undergo the significant changes depending on the cooling conditions. Such changes, undoubtedly, need to be taken into account in engineering developments and those improvements that are introduced from time to time into the planar technology.

Thus, a characteristic feature of the results obtained is that:

1) on the parameters r, n_e and m of annealed n-Si single crystals under specific conditions is significantly affected by the cooling rate of semiconductor objects from T_{ann} = 1200 ^{o}C the room temperature; such conditions are close to the practically used ones in planar technology of the manufacturing of semiconductor devices, including the integrated circuits and large-scale integrated circuits;

2) the most noticeable changes in the parameters ($r \approx 101.3$ %; $n_e \approx 43.9$ %; $m \approx 12.2$ %) of the annealed crystals (at 1200 ^{o}C during 2 h) do not occur at extremely high or low cooling rates ($u_{cl} \approx 1000$ or 1 ^{o}C/min); such changes occur at some intermediate value of cooling rate (the intermediate cooling rate of the crystals was equal $u_{cl} \approx 15$ ^{o}C/min in our case). This means that with monotonous cooling of the annealed crystal in an impurity-defective system the process occurs, which varies non-monotonically depending on the cooling rate in a wide range of cooling rates (from 1 to 1000 ^{o}C/min). In fact, this process is characterized by the presence of an extremum in the change of parameters, as evidenced by the most significant deviations in the values of the measured parameters, not only from analogous values in the initial samples, but also in the annealed crystals, which were cooled with extremely high and very low rates. The maximum of this function, undoubtedly, can not be directly related to $u_{cl} \approx 15$ ^{o}C/min, since we do not know its position between the limiting values of the cooling rates used in this work.

III. Comparison of the anisotropy parameters measured on n-Si ⟨P⟩ single crystals, doped with phosphorus impurity via the melt and by nuclear transmutation technique

Two groups of samples n-Si ⟨P⟩ (ordinary and transmutation-doped) were studied. The experimental studies were carried out on the samples that had the necessary crystallographic orientation (their length coincided with the direction [100]), which made it possible to measure changes in the resistivity ρ with pressure X, deducing the function $\rho(X)$ to saturation ($\lim_{X\to\infty} \rho(X) = \rho_\infty$).Such saturation was achieved under conditions $T = 77.4$ K, $\vec{X} \parallel \vec{J} \parallel [100]$ ($\vec{J}$ is the current) at $X \geq (0.6 \div 1.0)$ GPa and ensured the obtaining of the anisotropy parameter of electron mobility K in the framework of single isoenergetic ellipsoid according to the formula [26]

$$K = \frac{\mu_\perp}{\mu_\parallel} = \frac{3}{2}\frac{\rho_\infty}{\rho_0} - \frac{1}{2}, \tag{2}$$

where ρ_0 is the specific resistance at $X = 0$; $\mu_\parallel$, $\mu_\perp$ are the mobilities of charge carriers along and across the long axis of the isoenergetic ellipsoid, respectively.

The value of the anisotropy parameter of the electron-phonon drag thermo-emf M was determined from the formula [21]

$$M = \frac{\alpha_\parallel^{ph}}{\alpha_\perp^{ph}} = \frac{2K}{(2K+1)\frac{\alpha_0 - \alpha^e}{\alpha_\infty - \alpha^e} - 1} = \frac{2K}{(2K+1)\frac{\alpha_0^{ph}}{\alpha_\infty^{ph}} - 1}, \tag{3}$$

$$\alpha_0^{ph} = \alpha_0 - \alpha^e, \tag{4}$$

$$\alpha_\infty^{ph} = \alpha_\infty - \alpha^e, \tag{5}$$

where α_0^{ph}, α_∞^{ph} are the phonon components of the thermo-emf without pressure ($X = 0$) and in the saturation ($X \to \infty$), which are equal to the experimental data (α_0 and α_∞) without the electron (diffusion) component $\alpha^e = \frac{k}{e}\left[2 + \ln\frac{2\left(2\pi m^* kT\right)^{3/2}}{n_0 h^3}\right]$ (the Pisarenko formula); n_0 is the concentration of charge carriers; e is the electron charge; k is the Boltzmann constant; T is the temperature, h is the Planck constant; $m^* = N^{3/2}\sqrt[3]{m_\parallel m_\perp^2}$ is the effective mass of the density of states; N is the number of isoenergetic ellipsoids, in particular for n-Si $N = \begin{cases} 6 \text{ at } X = 0, \\ 2 \text{ at } X \geq 0.6 \text{ GPa} \end{cases}$; $m_\parallel$, $m_\perp$ are the effective masses along and across the long axis of isoenergetic ellipsoid, respectively.

For each of the samples the value of the anisotropy parameter of the drag thermo-emf M, which characterizes the phonon subsystem (see Table 4) was obtained from Eq. (3), using the experimentally measured (at $T \approx 85$ K) values of thermo-emf in undeformed (α_0) and deformed (α_∞) ordinary and transmutation-doped n-Si samples (with resistivity values at room temperature $\rho_{300K} \approx 200$ and 55 Ohm·cm), also releasing these data from contribution of the electron (diffusion) component of thermo-emf, in accordance with (4) and (5).

The results of the comparative experiments indicated that when the values of K coincided (within the limits of measurement errors), the value of the parameter M in transmutation-doped samples was significantly lower (~ 5), than in crystals doped with the same phosphorus impurity, but through a melt (~ 6.5) (see Table 4). This fact suggested that in the process of the standard technological annealing after transmutation doping (at ~ 800 °C during 2 h) the radiation defects is not completely eliminated. And these residual defects do not have a noticeable effect on the electronic subsystem, but significantly change the effects that occur with the participation of long-wavelength phonons. It could be assumed that the annealing of transmutation-doped crystals at higher temperatures with following sharp cooling can transform (if not completely, then at least partially) these residual defects into such point defects where phonons will be scattered less efficiently. Such process should be accompanied by an increase in the parameter M, which was confirmed in the experiments at study of the effect of high-temperature annealings and various cooling rates on the anisotropy parameters in n-Si samples doped with phosphorus by two different methods.

Two groups of n-Si ⟨P⟩ samples doped through the melt and by the nuclear transmutation method were studied. The values of the anisotropy parameters K and M were obtained both in the initial state, and after high-temperature annealing at 1200 °C during 2 h (and at two

Table 4

Comparison of the anisotropy parameters measured on n-Si crystals, doped with phosphorus impurity via the melt and by nuclear transmutation technique

ρ_{300K}, Ohm·cm	$n_{e\,77.4K} \cdot 10^{-13}$, cm^{-3}	$\mu_{77.4K} \cdot 10^{-4}$, cm^2/V·s	K	M	Doping method
200	1.9	1.95	5.4	6.6	Cz
200	1.7	2.05	5.6	4.8	Slow neutrons
55	5.7	1.90	5.3	6.4	Cz
55	5.7	2.15	5.4	4.9	Slow neutrons

Table 5

Effect of high-temperature annealing and various cooling rates on the anisotropy parameters in n-Si crystals doped by of different methods

n-Si samples		$n_{e\,77.4K}\cdot10^{-13}$, cm^{-3}	$m_{77.4K}\cdot10^{-4}$, $cm^2/V{\cdot}s$	K	M	Doping method
Initial		5.50	1.95	5.25	6.30	Cz
1200 °C, 2 h	1000 °C/min	5.65	2.00	5.20	5.70	
	1 °C/min	5.10	2.00	5.25	5.20	
Initial		5.72	2.14	5.25	5.40	Slow neutrons
1200 °C, 2 h	1000 °C/min	5.92	2.05	5.55	7.60	
	1 °C/min	5.10	2.00	5.50	7.20	

cooling rates from the annealing temperature to the room temperature). The results of these experiments with subsequent averaging are summarized in Table

In the crystals of the different doping method the anisotropy parameter of mobility is practically unchanged $K = 5.20 \div 5.55$ (при 77.4 K), according to the data in Table 5. At the same time, the anisotropy parameter of thermo-emf M reacts differently on the thermal annealing with consequent cooling. In samples doped through the melt, the parameter M exhibits a certain tendency to decrease by ~ $10 \div 17$ % (from 6.3 to $5.7 \div 5.2$), whereas in the transmutation-doped samples the value of this parameter increases by $30 \div 40$ % (from 5.4 to $7.2 \div 7.6$). Thus, the scattering centers for long-wavelength phonons were eliminated by the high-temperature treatment of transmutation-doped n-Si, as a result of which the probability of scattering of phonons decreased, whereas tenso-thermo-emf and anisotropy of thermo-emf increased sharply.

It should be noted that in experiments with transmutation-doped crystals the similar behavior of the anisotropy parameters K and M was also observed under high-temperature annealing of a longer duration (T_{ann} = 1200 °C during 72 h).

The analysis of the data obtained (see Table 5) shows that in experiments with both ordinary and transmutation-doped samples the values of the anisotropy parameter of mobility practically do not undergo the appreciable changes within the limits of measurement accuracy under used thermal annealings and two cooling rates. The high-temperature annealing of n-Si crystals doped with phosphorus through the melt leads to some decrease in the thermo-emf anisotropy parameter, and these changes were more pronounced with slow cooling. In contrast to the ordinary crystals the similar annealing of silicon crystals doped by the nuclear transmutation method leads to an increase in the value of the thermo-emf anisotropy parameter by about 1.5 times, and the effect was more pronounced with rapid cooling. The differences found in the change of the thermo-emf anisotropy parameter for samples of various doping methods can be explained by the presence of the residual radiation defects in the transmutation-doped crystals. Such defects, in fact, can not be completely eliminated by technological annealing. In crystals doped through the melt, such defects are in principle absent.

A more detailed discussion of the mechanisms of those processes that can occur at thermal annealings, on basis of the results given only, would be probably ill-founded, since in the investigated crystals the concentrations of the so-called low-activity impurities (such as carbon or impurities of inert gases) were not known to us. Although the presence of such impurities in the volume of crystals may affect to a certain extent on the results obtained.

Більш детальне обговорення механізмів тих процесів, що можуть відбуватися при термовідпалах, на основі лише наведених результатів було б, напевне, мало обгрунтованим, оскільки у досліджуваних кристалах концентрації так званих малоактивних домішок (типу вуглецю або домішок інертних газів) не були відомими. А від наявності в об'ємі кристалів таких домішок приведені результати можуть бути в певній мірі залежними.

Conclusions

In n-Si ⟨P⟩ crystals of various growing (Cz, FZ) and doping methods (through a melt, by nuclear transmutation) the features of changes in the most important electrophysical and thermoelectric parameters have been investigated under the influence of high-temperature annealings (1200 °C; 2 and 72 h) and several cooling rates ($u_{cl} \approx 1, 15, 1000$ °C/min).

In Cz-Si samples enriched with oxygen impurities, at the thermal annealings with consequent cooling at the rates of 1 and 1000 °C/min, it was revealed the tendency to decrease of the charge carrier concentration, which is characteristic both for low-resistance (ρ_{300K} = 0.5 Ohm·cm), and for high-resistance (ρ_{300K} = 80 Ohm·cm) samples. Meanwhile in the investigated samples the changes in the values of mobility are oppositely directed: the mobility in low-resistance samples shows a tendency to grow, and in high-resistivity samples it decreases. Seemingly, the increase in the mobility of charge carriers is due to the temperature "destruction" of the thermodonors.

In silicon crystals ($\rho_{300K} \approx 15$ Ohm·cm), doped in ordinary way (through a melt) and by nuclear transmutation, the oppositely directed tendencies in the mobility change after thermal annealings are found: in ordinary crystals there is a tendency to decrease, whereas in transmutation-doped – to growth. The increase in the mobility after high-temperature annealing is probably due to a more complete annealing of those defects that were not completely eliminated in the process of the standard technological annealing after neutron transmutation doping.

It is established that with the coincident values of the mobility anisotropy parameter (in the limits of measurement errors) in silicon crystals of both doping methods, the values of the thermo-emf anisotropy parameter in the transmutation-doped crystals will be significantly much lower, than in the ordinary crystals. In this case, the residual (not completely removed in the process of technological annealing) defects in the transmutation-doped silicon crystals do not reduce the values of the charge carrier mobility.

It was revealed that high-temperature annealing in the ordinary silicon crystals leads to a certain decrease in the value of the thermo-emf anisotropy parameter, which is more pronounced with slow cooling of the samples, whereas in the transmutation-doped crystals the values of this parameter increase by about 1.5 times, and this effect is more pronounced with rapid cooling. It was found that with the used heat treatments the mobility anisotropy parameter in crystals of both methods of doping remains practically unchanged.

The most significant influence of cooling at the intermediate value of the cooling rate (15 ^{o}C/min) after high-temperature annealing on the specific resistance, concentrations and mobilities of charge carriers in the transmutation-doped silicon crystals was established. This fact indicates about the nonmonotonic character of the processes of the interdefect interaction in crystals under their monotonic cooling, and causes the presence of the extremum in the change of the Hall parameters.

Gaidar G.P. **-** Doctor of Physics and Mathematics, Senior Researcher, Head of the Department of Radiation Physics..

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Г.П. Гайдар

Вплив термовідпалів і способів охолодження на електрофізичні параметри n-Si, легованого домішкою фосфору через розплав і методом ядерної трансмутації

Інститут ядерних досліджень НАН України, пр. Науки, 47, Київ, 03680, Україна, e-mail: gaydar@kinr.kiev.ua

У роботі досліджено вплив різних режимів термообробки на кінетику електронних процесів у кристалах кремнію, легованих домішкою фосфору через розплав та методом ядерної трансмутації. Встановлено найбільш значний вплив охолодження при проміжному значенні швидкості охолодження ($u_{охол} \approx 15$ ^{o}C/хв) після високотемпературного відпалу на основні електрофізичні параметри трансмутаційно легованих кристалів n-Si ⟨P⟩. Виявлено і пояснено особливості змін параметрів анізотропії рухливості і термоерс, виміряних на кристалах кремнію різних способів легування, як у вихідному стані, так і після високотемпературного відпалу при використанні різних швидкостей охолодження.

Ключові слова: електрофізичні параметри, n-кремній, способи легування, параметри анізотропії, термічний відпал, швидкість охолодження.